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LOCALIZED ELECTRONS IN TETRAGONAL $YBa_2Cu_{2.93}O_{6.38}$

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ABSTRACT

The structure refinement of tetragonal $YBa_2Cu_{2.93}O_{6.38}$ has been carried out with the final R-value of 0.019 (R_w=0.020) by X-ray single crystal diffraction method. Difference Fourier maps reveal the existence of localized electrons around Cu and Ba atoms in the unit cell.

INTRODUCTION

The 1986 Bednorz and Müller's report[1] awoke intensive studies on ceramic superconductor in the La-Ba-Cu-O and Y-Ba-Cu-O systems[2,3]. Since it has been reported that $YBa_2Cu_3O_7$ definitely exhibits the highest critical temperature T_c above liquid nitrogen temperature, most of the researchers have devoted themselves to the study of the Y-Ba-Cu-O system[4,5,6]. Recently, Maeda et al. and Chu et al. have discovered independently new ceramics in the Bi-Sr-Ca-Cu-O and Bi-Sr-Ca-Cu-Al-O systems[7,8] which show a T_c of about 105K. This discovery suggests the potential existence of further more new oxide superconductors with higher T_c. The search for new materials has made remarkable progress while the phenomenon of superconductivity seems not to be still understood. In order to improve the understanding of this phenomenon, it is necessary to obtain details and precise information on the crystal structure and electron distribution for each superconductive material. The outlines of the

$YBa_2Cu_3O_7$ crystal structure were reported previously[9-13] but no information on the electron distribution around the metallic atoms is available.

By using a good quality single crystal large enough to make a spherical shape for accurate X-ray diffraction intensity measurements, the precise structure refinement of $YBa_2Cu_{2.93}O_{6.38}$ was carried out. This report shows the results of the structure analysis done with the final R value of 0.019. The well refined crystal structure reveals the electron distribution around Ba and Cu atoms with peak heights of 1.5 e/A^3.

EXPERIMENTAL

Good quality $YBa_2Cu_{2.93}O_{6.38}$ single crystals were synthetized by the growth method[14]. Tetragonal single crystals were grown in nonstoichiometric Ba-Y-Cu-O melts. A mixture whose composition corresponds to $2BaO:Y_2O_3:2CuO$ = 12:1:26 (mole ratio) was calcinated in air at 850°C and then heated slowly up to 1000°C. The melt was maintained at this temperature during 3 hours. An alumina rod had been inserted slightly underneath the surface of the melt. Then, the melt was cooled down at the rate of 10°C per hour. When the temperature reached 880°C, the crucible was removed in order to pour out the residual melt. As a result, single crystals with well developed rectangular shape grew on the surface of the alumina rod. As-grown single crystals were about 0.5 mm in length and have black lustrous surfaces. Electron probe microanalysis showed that the grown cystals were a monophase of $YBa_2Cu_3O_7$.

A single crystal whose dimensions were of 0.2 x 0.2 x 0.2 mm was rounded under an optical microscope to a sphere of 0.12 mm in diameter after its structural purity had been checked by X-ray. The crystal symmetry and cell dimensions of this spherical crystal was determined by the X-ray camera method. Precession photographs gave preliminary the following crystal data. The possible space groups are P42m, P4m2 P222, P4mm and P4/mmm because the intensity distributions on X-ray films shows tetragonal symmetry with the Laue group of 4/mmm and no systematic absence appeared. The cell dimensions are a=3.86A, c=11.81A and V=176.0A.

The X-ray diffraction intensity data in three dimensions were collected on a Rigaku AFC-5 four-circle X-ray automatic diffractometer with the MoKα radiation (λ=0.71069A) monochromatized by graphite. The 2θ-ω scanning technique was employed for the X-ray data collection up to 2θ=110°. The 2θ-ω scanning speed was 2 deg./min. and the width was 1.2 + 0.5 tan θ.

A total of 5976 reflections were measured and 750 reflections greater than $3\alpha_F$ were used for structure refinements after averaging all equivalent reflections. 4510 reflections greater than $3\alpha_F$ were used for the refinements assuming a lower symmetry. The precise cell dimensions were calculated by the least-squares method using the high-angle 2θ values of 50 reflections which were measured carefully with a Rigaku AFC-5 four-circle automatic diffractometer with the $MoK_{\alpha 1}$ radiation (λ=0.70926A). The refined cell dimensions were a=3.860 (1) A, c=11.813 (4) A and V=176.05 (7) A^3. After the correction for Lorenz and polarization effects, all necessary crystallographic calculations including spherical absorption correction were carried out using the crystallographic computer program RADY[15] on a FACOM M360 MP computer at the Photon Factory. The atomic scattering factors were taken from the X-ray crystallography International Table (1974).

RESULTS

At the first stage of structure analysis, the Patterson and Fourier syntheses were made to find the atomic positions of heavy atoms like Y, Ba, and Cu. The difference Fourier synthesis was done in order to find the positions of oxygen atoms. The structural refinements were carried out by varying the parameters of atomic coordinates, atomic site occupancies, and temperature factors. At the final refinement, all parameters converged well with R=0.019 (R_W=0.020). Very good coincidence between observed F_o and calculated F_c as shown partially in Table 1 was obtained. The final atomic parameters are given in Table 2 and the temperature factors in Table 3.

The crystal structure is shown in Figure 1. It is closely related to the pervoskite type. It is very interesting to see that the site occupancy of 02 is 0.190 and that there is no difference in site occupancy between oxygen atoms at the positions of ($\frac{1}{2}$ 0 0) and (0 $\frac{1}{2}$ 0) in tetragonal $YBa_2Cu_{2.93}O_{6.38}$. However, there is a distinct difference of site occupancies between both oxygen atoms in the structure of orthorhombic $YBaCu_{3-x}O_{7-y}$. The Cu atoms in Cul sites are slightly deficient, while the Cu2 sites are fully occupied. Table 4 gives the bond distances and angles of the tetragonal $YBa_2Cu_{2.93}O_{6.38}$ at the final refinement.

DISCUSSION

The information on the actual electron distribution in $YBa_2Cu_{2.93}O_{6.38}$ could be very useful to understand electronic mechanisms for superconducting pairing[16-17]. In order to find out the electron distributions in this

TABLE 1 - COMPARISON OF F_o AND F_c* OF FINAL REFINEMENT

Index	F_o	F_c	Index	F_o	F_c
100	36.55	-35.03	310	117.94	116.62
200	199.35	192.83	410	25.30	-25.57
300	29.85	-29.27	510	71.80	71.51
400	114.02	110.94	610	16.87	-16.81
500	22.88	-22.57	710	44.99	43.19
600	68.52	67.15	810	9.23	-8.68
700	13.85	-13.69	910	27.21	26.36
800	42.83	42.03	220	156.86	152.19
900	6.95	- 6.97	320	27.45	-27.61
110	165.09	172.22	420	99.39	98.18
210	31.48	-30.67	520	20.86	-20.73

* The whole tables of F_o-F_c are available from the author (Z.I.) upon request.

TABLE 2 - ATOMIC PARAMETERS OF TETRAGONAL $YBa_2Cu_{2.93}O_{6.38}$

Atom	Number of Positions	Wyckott Notation	Site Occupancy	x	y	z
Ba	2	h	0.9993(4)	½	½	0.19438(8)
Y	1	d	1.0014	½	½	½
Cu1	1	a	0.933 (2)	0	0	0
Cu2	2	g	1.000 (1)	0	0	0.36084(2)
O1	2	g	1.000	0	0	0.1532 (1)
O2	2	f	0.190 (5)	0	½	0
O3	4	i	1.000	½	0	0.37921(7)

TABLE 3 - THERMAL PARAMETERS OF $YBa_2Cu_{2.93}O_{6.38}$

Atom	β_{11}	β_{22}	β_{33}	β_{eq}*
Ba	0.01000(3)	-	0.001255 (1)	0.631 (1)
Y	0.00517(7)	-	0.000985 (1)	0.387 (2)
Cu1	0.0155 (3)	-	0.001138 (2)	0.827 (3)
Cu2	0.00401(6)	-	0.001460 (1)	0.431 (1)
01	0.0225 (6)	-	0.001506 (8)	1.17 (1)
02	-	-	-	1.4 (1)**
03	0.0031 (3)	0.0075 (4)	0.001785 (6)	0.54 (2)

* B_{eq} is an equivalent isotropic temperature factor derived from β_{ij} which is defined by:
$\exp\{(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2kl\beta_{13}+2kl\beta_{23})\}$.

**An isotropic temperature factor was assumed for the 02 atoms

TABLE 4-INTERATOMIC DISTANCES AND ANGLES OF $YBa_2Cu_{2.93}O_{6.38}$

Bond	Distances (A)	Bond	Angles (degree)
Cu1-01	1.809 (1)	02-01-02	62.11 (3)
Cu1-02	1.930 (1)	03-01-03	48.94 (2)
01 -02	2.645 (1)	03-Cu2-03	89.28 (0)
Cu2-01	2.453 (1)	01-Ba-01	88.23 (2)
Cu2-03	1.942 (1)	01-Ba-02	54.38 (2)
01 -03	3.294 (1)	01-Ba-03	70.77 (3)
Ba -01	2.772 (1)	02-Ba-02	54.12 (1)
Ba -02	2.999 (0)	02-Ba-03	98.48 (2)
Ba -03	2.914 (1)	03-Ba-03	82.95 (2)
Y -03	2.400 (1)	03-Y -03	107.05 (3)
		03-Y -03	78.05 (3)

crystal, the difference Fourier maps were made using the difference of $|F_{obs}| - |F_{calc}|$ which came from the final step of structure refinement. Atomic scattering factors for the spherical model were used in the calculation of the difference Fourier. The difference Fourier map of (100) section at $z=\frac{1}{2}$ gives the information on electron distribution around Y and Ba atoms as shown in Figure 2. The highest-positive and the lowest-negative peaks were found around Ba atoms with peak heights of ± 1.5 e/A^3. These residual density peaks of electrons may be caused by the thickest electron cloud of Ba atoms.

The difference Fourier map of (100) section at z=0 reveals the existence of localized electron distributions around Cu atoms as shown in Figure 3. It was found that there is a pair of residual density peaks of Cu2 atoms located 0.92A above and below the Cu2 atoms along the c-axis, while there is no residual peaks around Cu1 atoms. Cu1 atoms have spherically distributed electrons and should be in an univalent oxidation state where the 3d orbits of electrons are fully occupied. On the other hand, the localized electron distributions around Cu2 are considered to be coming from d-electrons of Cu2 atoms, because the distance from the center of a Cu2 atom to that of residual electron peak would be the same as the radius of d-electrons. This localized Cu2 3d electrons suggests a divalent or trivalent ionic state where the Cu atoms have unoccupied 3d electron orbits. Taking into account the fact that X-ray photoelectron observations and XANES spectra [18-19] suggests the absence of a trivalent state of Cu atoms, the ionic state of Cu2 can be considered as divalent[20].

The exact mechanism responsible for superconductivity has not been proposed yet. Therefore, it is believed that this study about electron distribution in $YBa_2Cu_{2.93}O_{6.38}$ will provide useful information to establish the theory of superconductivity.

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LIST OF FIGURE CAPTIONS

Figure 1 Crystal Structure of Tetragonal $YBa_2Cu_{2.93}O_{6.38}$. The largest circles correspond to the oxygen atoms, the medium ones to yttrium and barium atoms and the smallest to the copper atoms.

Figure 2 A difference Fourier map of the ( )0) section at Z=½ in tetragonal $YBa_2Cu_{2.93}O_{6.38}$. Contours are at intervals of 0.2 e/A^3. Negative contours are in broken lines and zero contours being omitted.

Figure 3 A difference Fourier map of the (100) section at z=0 in tetragonal $YBa_2Cu_{2.93}O_{6.38}$. Contours are done at the same level as indicated in Figure 2.

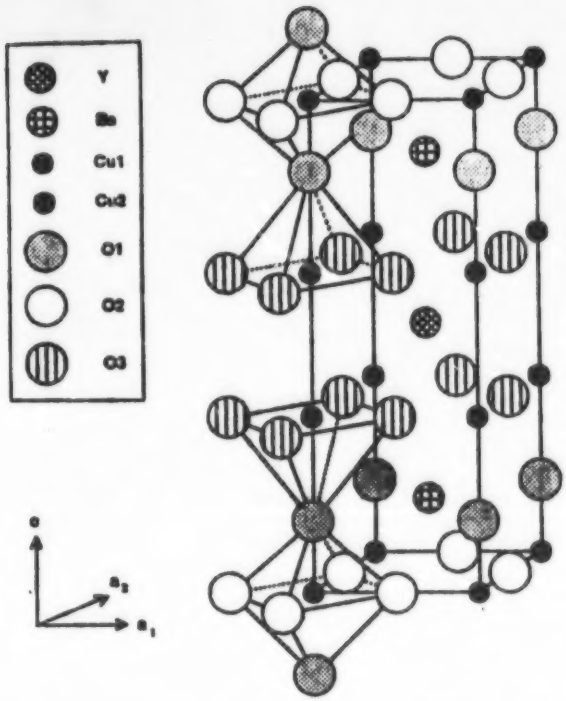

Fig 1

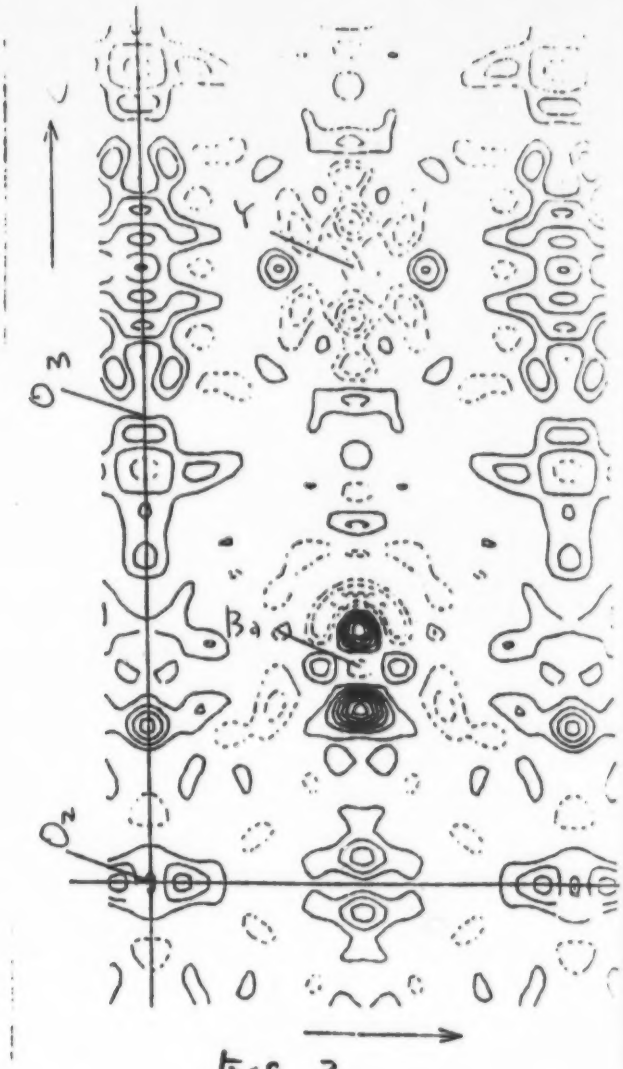

Fig 2

Fig 3